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This proposal addresses the nacre in the abalone shell and the methods that will be taken to fabricate and test a bioinspired material based on its structure. Our objectives are 2-fold: (1) to fabricate a nano/micro-laminate that mimics the nacre in the abalone shell using engineering ceramic compositions and (2) to test these laminates and determine modes of fracture and energy absorption. The main focus is to distinguish the role of mineral bridges, organic ligament stretching and asperities on the toughening behavior.

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Report Title

Final report: Synthesis of nacre-like structures using novel fabrication techniques

ABSTRACT

This proposal addresses the nacre in the abalone shell and the methods that will be taken to fabricate and test a bioinspired material based on its structure. Our objectives are 2-fold: (1) to fabricate a nano/micro-laminate that mimics the nacre in the abalone shell using engineering ceramic compositions and (2) to test these laminates and determine modes of fracture and energy absorption. The main focus is to distinguish the role of mineral bridges, organic ligament stretching and asperities on the toughening behavior.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

L. Tombolato, E. Novitskaya, P.-Y. Chen, F.A. Sheppard and J. McKittrick, "Microstructure and elastic and fracture properties of horn keratin," Acta Biomater., 6, 319–330 (2010).

J. McKittrick, P.-Y. Chen, L. Tombolato, E. Evdokimenko, W. Trim, E.A. Olevsky, M.F. Horstemeyer and M.A. Meyers, "Review: Energy absorbent natural materials and bioinspired design strategies," Mater. Sci. Eng. C (in press).

M.E. Launey, P.-Y. Chen, J. McKittrick and R.O. Ritchie, "Mechanistic aspects of fracture and R-curve behavior in elk antler bone," Acta Biomater., (in press).

Number of Papers published in peer-reviewed journals: 3.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

J. McKittrick, "Structural biological materials: Fascinating insights into the structure of life, UC Riverside, Riverside, CA, March 6, 2009.

E. Evdokimenko, L. Tombolato, P.Y. Chen, F. Sheppard and J. McKittrick, "Structure and mechanical properties of horn keratin," UCSD Research Expo, March 26, 2009.

J. McKittrick, "Structural and mechanical properties of the nano-constituents in cancellous bone," First International Conference on Nanostructured Materials and Nanocomposites
Kottayam, Kerala, April 6, 2009.

P.-Y. Chen, R. Kulin, F. Jiang, F. Sheppard, J. Curiel, K.S. Vecchio and J. McKittrick, " Quasi-static and dynamic fracture behavior of antler and bone: A comparative study," Materials Research Society Spring Meeting, San Francisco, CA, April 16, 2009.

J. McKittrick, "Soft biological materials: Role in the mechanical properties of biological composites," 1st International Conference on Soft Materials, Shanghai, China, May 25, 2009.

J. McKittrick and P.Y. Chen, "Materials science research studies on bone and biomineralization," Centro de Nanociencias y Nanotecnologia, Ensenada, Mexico, June 25, 2009.

J. McKittrick, P.-Y. Chen, D. Toroian and P. Price, "Bone: A natural nanocomposite," 17th Annual International Conference on ? Composites/Nano Engineering, Honolulu, HI, July 26, 2009.

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.A. Hirata, S.P. Diaz, P.-Y. Chen, M.A. Meyers and J. McKittrick, “Bioinspired inorganic/polymer thin films,” MRS Proceedings, Fall Meeting 2009 (in press).

P.-Y. Chen, D. Toroian, P.A. Price and J. McKittrick, “Structural and mechanical properties of the collagen-mineral nano-constituents in cancellous bone,” Proceedings of the 1st International Conference on Nanostructured Materials and Nanocomposites, Kottayam, India, April 6-8, 2009.

P.-Y. Chen, F.A. Sheppard, J.M. Curiel, J. McKittrick. Fracture mechanisms of bone: A comparative study between antler and bovine femur bone. Materials Research Society Symposium Proceeding, Fall 2008, Volume 1132E, Symposium Z1.4.

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Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Po-Yu Chen	0.25
FTE Equivalent:	**0.25**
Total Number:	**1**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Joanna McKittrick	0.10	No
Marc Meyers	0.10	No
FTE Equivalent:	**0.20**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	2.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME	
Jerry Curiel	
Fred Sheppard	
Total Number:	**2**

Names of personnel receiving PHDs

NAME	
Po-Yu Chen	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

FORWARD

The extraordinary mechanical properties such as hardness, strength and toughness that abalone shell develops in a natural way by arranging ~ 500 nm thick inorganic $CaCO_3$ (aragonite) and organic layers of ~ 50 nm have inspired many researchers around the world to develop novel composites following this inorganic/organic heterostructure [1-4]. Nacre in the abalone shell has a well-defined arrangement of oriented aragonite hexagonal tiles (90 vol.%) held together by a biopolymeric phase (10 vol.%) in a brick and mortar structure, as shown in Figure 1. The fracture resistance of nacre is through energy absorption mechanisms of crack diversion accomplished by tile pullout. The interface between the aragonite tiles and the organic has nanostructural features such as mineral bridges and nanoasperities that help resist this pullout. The work of fracture of nacre has been reported to be 3000X that of the mineral phase [5], resulting in widespread interest in fabricating bioinspired materials based on the design of nacre.

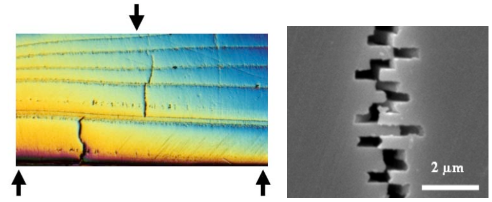

Figure 1. (a) Tortuous crack growth in abalone nacre and (b) fracture path occurs through tile pullout.

Besides the interfacial features, another important consideration is the volume fraction of the organic phase. Typically, synthetic laminated ceramic composites contain a substantial fraction of a ductile phase and designs based on thin layers of polymers are not expected to have much fracture resistance. However, Mayer [6] showed that simple Al_2O_3 beams glued with a thin polymer adhesive had a work of fracture that increased as the volume fraction of the adhesive decreased, indicating that more complex fractures modes were operating with a small volume fraction of the polymer phase.

Bioinspired synthesis of nacre-like structures has been performed through dip coating of Al_2O_3/epoxy [7] or clay/polyelectrolytes [4] that produced laminates with oriented particles. The Al_2O_3/epoxy had a work of fracture and shear strength greater than that of pure Al_2O_3 [7] while the clay/polyelectrolyte composites had a tensile strength similar to nacre [4]. Combining chemical bath deposition of oxides with layer-by-layer assembly of organic polymers has been used to prepare TiO_2/polymer multilayer composites [4]. Interestingly, the hardness and Young's modulus slightly increased in comparison to the monolithic oxide films. Tomsia et al. [1,3] have produced innovative Al_2O_3-PMMA structures by suspending ceramic particles in water and then freezing the system in a controlled thermal gradient. A laminated structure resulted, including 'mineral bridges' that formed from dendrites that grew perpendicular to the main growth direction. The Al_2O_3-PMMA had a fracture toughness of ~ 30 $MPam^{1/2}$, a factor of 10x that of Al_2O_3, indicating that the fracture resistance of ceramic can be greatly improved by fabricating nacre-like structures. These reports illustrate that bioinspired synthesis of nacre-like structures have excellent potential to form highly fracture resistant materials.

STATEMENT OF PROBLEM STUDIED

Our goal is to fabricate nacre-like structures using synthetic materials and examine the microstructure and mechanical properties. We chose two physical vapor deposition methods in order to prepare zirconium nitride (ZrN) and polymethylmethacrylate (PMMA) multilayer composites with volume fractions of the constituent phases the same as nacre. Table I compares the structure properties of nacre and the synthetic constituents. The Young's moduli and hardness values of both ZrN and PMMA are larger than their natural counterparts, suggesting that laminates built with these materials should have superior mechanical properties. For the ZrN thin films we employed DC magnetron sputtering of zirconium metal while the PMMA polymeric layers were produced by pulsed laser deposition (PLD) [9], sequentially, in the same growth chamber without breaking the vacuum.

Table I. Comparison of nacre and synthetic constituents

Composition	Structure	Young's modulus (GPa)	Density (gm/cm^3)	Hardness (GPa)
ZrN	Rock salt a = 0.458 nm	460	7.09	23
$CaCO_3$ (aragonite)	Orthorhombic a = 0.496, b = 0.797, c = 0.574 nm	70	2.83	0.61
PMMA	$[C_5O_2H_8]_n$	3	1.19	0.22
Nacre organic	Chitin and various proteins	<1	~1.1	

EXPERIMENTAL DETAILS

Thin film growth

ZrN films were fabricated by DC reactive magnetron sputtering, as shown in Figure 2. The deposition was carried out in a laboratory-built high vacuum system equipped with both mechanical and turbomolecular pumps that reach a background pressure of 5 X 10^{-6} Torr. A Zr disc (99.998%) was used as the target (33 mm diameter, 5 mm thickness) and Si (100) was used as the substrate. The target-substrate distance was 8 cm, a fixed DC power of 100 W was used and the substrate temperature during deposition was kept at 130ºC (for reasons of the subsequent polymer deposition). The sputtering gas (Ar) flow was 3 sccm and the reactive gas (N_2) flow was 0.9 sccm. The partial pressure during the deposition was maintained at 3 mTorr. The growth rate under these conditions was ~ 50 nm/min. After the ZrN film was deposited, the chamber was evacuated for PLD of the PMMA layers.

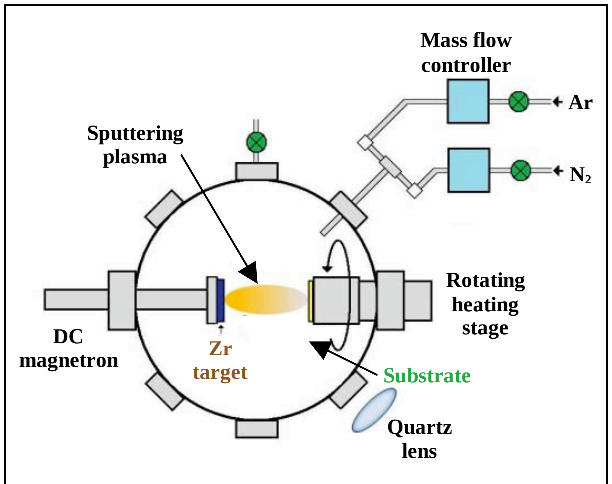

Figure 2. Schematic diagram of the DC magnetron sputtering for deposition of the ZrN thin films.

A retractable arm with the PMMA target was lowered into the chamber, blocking the Zr target (Figure 3), which is equipped with a port for a laser, which was used for the deposition. An excimer laser beam (KrF, λ = 248 nm, 10 ns pulse duration) with a fluence energy in the range of 400-1000 J/cm^2 was focused on a hot pressed transparent PMMA target (Goodfellow medical grade). The laser fluence was calculated by dividing the measured integral laser energy by the blackened area on a photosensitive paper. The growth rate was very rapid – about 20 sec was required to deposit a 60 nm thick film.

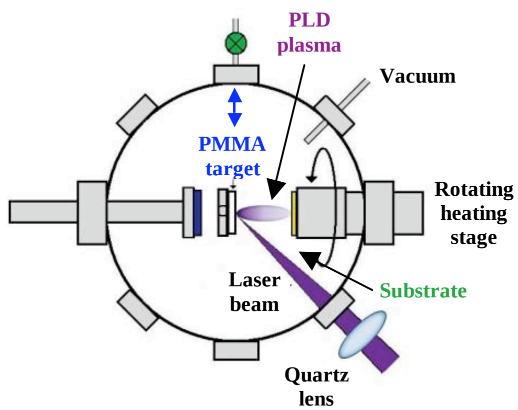

Figure 3. Schematic diagram of the PLD mode for deposition of the PMMA thin films. During the PMMA experiment the Ar and N_2 valves are closed.

By combining these two techniques (DC-sputtering followed by PLD) and using the same chamber without breaking vacuum, we have fabricated ZrN/PMMA multilayer composites on (100) silicon substrates.

RESULTS AND DISCUSSION

Structural and morphological characterization of the films

The ZrN films were characterized by x-ray diffraction (XRD) in a Philips X'pert diffractometer with CuK$_\alpha$ (λ= 0.154 nm) radiation. Figure 4 shows representative XRD pattern of a ZrN film deposited on with a substrate temperature, T_s = 130˚C. A random orientation of grains is observed, showing the (111), (200) and (220) crystallographic reflections of the face-centered

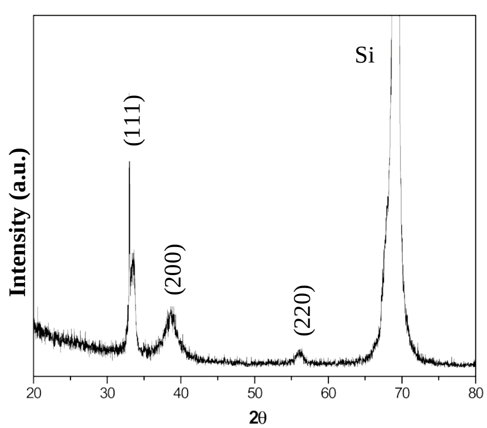

Figure 4. XRD pattern of cubic ZrN on Si (100) substrate.

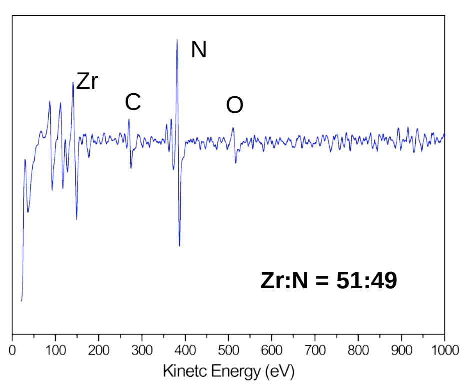

Figure 5. AES spectrum of the as-deposited ZrN film.

cubic ZrN lattice. This is an unusual result for a ceramic which is usually amorphous or weakly crystalline in the as-deposited condition under this low deposition temperature. Auger electron spectroscopy (Figure 5) reveals that a film with Zr:N of 51:49 was achieved and the only peaks identified are those of Zr , N and C and O. The carbon and oxygen is likely due to contamination from the atmosphere when transferring the film to the spectrometer.

Atomic force microscopy (AFM) studies show the films to be very smooth with a RMS surface roughness of 1.23 nm, as shown in Figure 6. Although nacre has nanoscale features at the inorganic/organic interface that provide resistance to tile separation, these extremely smooth surfaces, and their subsequent roughening, can be used to determine the influence of surface roughness on fracture resistance of ceramic/polymer laminates.

An SEM cross-sectional micrograph of a 1 μm thick film is shown in Figure 7. The film is dense and has uniform thickness and the columnar growth of the crystallites is observed, similar to the oriented growth of aragonite in nacre. More oriented films could be obtained with a change in substrate material, better mimicking the nacre struture.

The PMMA films were deposited on a substrate heated to 130˚C. This temperature was selected from DTA measurements where a loss < 1 wt.% occurred at this temperatures. The substrate temperature was minimized for the deposition of the polymer while being maximized (as much as possible) to promote well-crystallized ceramic films. The cross-sectional section of a film 1 μm thick (Figure 8) shows a featureless morphology with a uniform thickness.

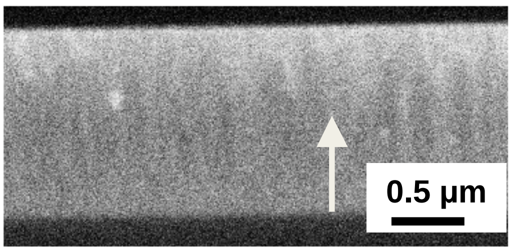

Figure 7. SEM image of a ZrN film, 1 μm thick, showing columnar growth.

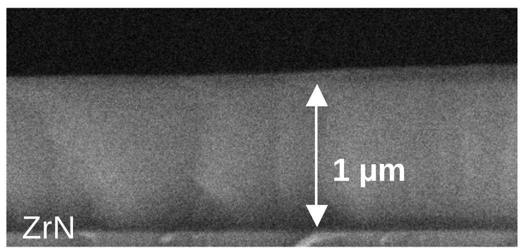

Figure 8. PMMA film deposited on a ZrN film.

Multilayer deposition

Surface morphology and cross sectional micrographs were analyzed by scanning electron microscopy (SEM) in a JEOL JSM-5300 SEM. In Figure 9, shown is an SEM micrograph of fracture cross-section of a five laver ZrN separated by four layers of PMMA. The PMMA thickness ranged from 30-90 nm while the ZrN thickness was maintained at ~ 1 μm, which resulted in a ceramic/polymer ratio of nacre. This illustrates that this sequential deposition technique can be used to fabricate uniform, nacre-like structures.

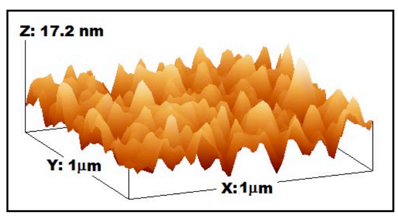

Figure 6. AFM scan of the ZrN film with a surface RMS roughness of 1.23 nm.

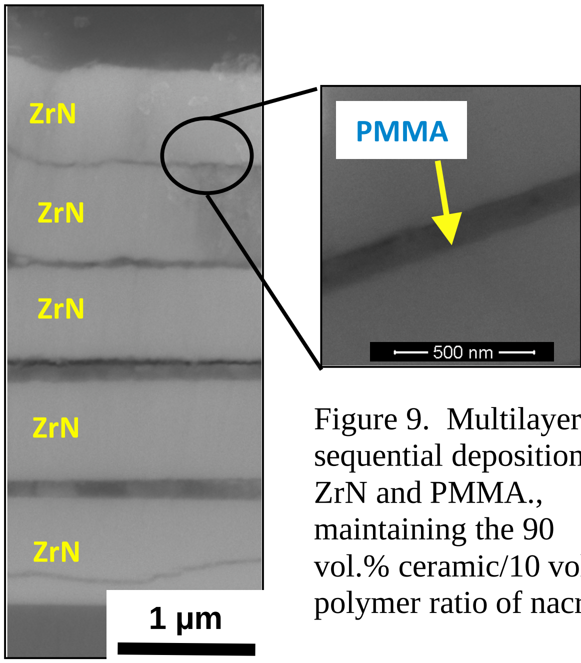

Figure 9. Multilayer sequential deposition of ZrN and PMMA., maintaining the 90 vol.% ceramic/10 vol.% polymer ratio of nacre.

There are several ways to introduce nanoscale structures at the ceramic/polymer interface. One is to increase the power of the sputtering gun, which would roughen the ZrN surface, producing nanoasperities. One method to fabricate mineral bridges is to pulse the laser on the DC magnetron sputtered nitride films. At a sufficient fluence, the laser pulse will produce the well-known splatter patterns that are typical on the surface of a PLD film. These splatter patterns have substantial height – enough so to bridge one ZrN layer to the next through the PMMA film, thereby creating the mineral bridges.

Nanoindentation

Nanoindentation measurements were taken in a Hysitron Ubi1 nanomechanical testing system (Hysitron Inc.) in conjunction with a Veeco Dimension 3100 AFM Nanoscope IV system (Veeco Metrology Group). The Hysitron nanoindenter monitors and records the load and displacement of the indenter, a diamond Berkovich three-sided pyramid, with a force resolution of at least 2.0 nN and displacement resolution of 0.1 nm. Hardness and elastic modulus were obtained from the recorded load-displacement curves. The indentation impressions were then imaged *in situ* by using the indenter tip. A series of 6-9 indentations were performed for each sample.

Nanoindentation hardness is defined as the indentation load divided by the projected contact area of the indentation. It is the average pressure that a material will support under load. From the load-displacement curve, hardness can be obtained at the peak load as:

$$H = \frac{P_{\max}}{A}$$

where P_{max} is the maximum load and A is the projected contact area. For an indenter with known geometry such as the Berkovich tip used in this study, the projected contact area is a function of the contact depth, which is measured by the nanoindenter *in situ* during indentation [10-12]. Therefore, the projected area A can be measured and calculated directly from the indentation displacement.

Representative load-displacement curves made at a maximum load of 10.5 mN on the ZrN thin film is illustrated in Figure 10. The penetration depth (or displacement) at the maximum load was h_{max} = 155.81 nm. Similar hardness values (H ~ 20 GPa) were obtained for a single ZrN film and the ZrN(3)/PMMA(2) multilayer samples as can be observed in Figure 11, which plots the extracted hardness as a function of displacement. These values are similar to other published values of bulk and thin film ZrN [13].

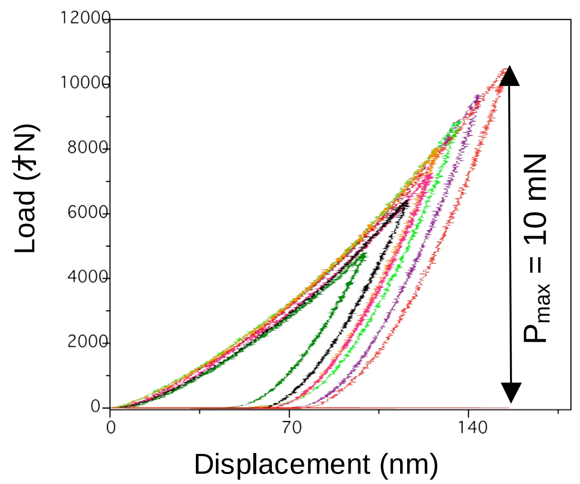

Figure 10. Representative load-displacement curve measured on a ZrN film by nanoindentation.

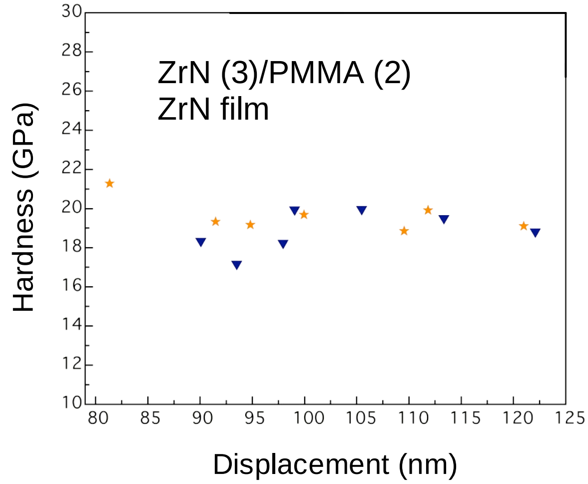

Figure 11. Hardness of a single ZrN film and a 3 layer ZrN/ 2 layer PMMA multilayer structure.

The elastic modulus was calculated using the Oliver-Pharr data analysis procedure [14] beginning by fitting the unloading curve to a power-law relation. The unloading stiffness can be obtained from the slope of the initial portion of the unloading curve, *S* (Figure 10) [14]:

$$S = \left.\frac{dP}{dh}\right|_{elastic}$$

$$S = \frac{2}{\sqrt{\pi}}\frac{E}{1-\nu^2}\sqrt{A}$$

where ν is the Poisson's ratio.

The elastic modulus as a function of the number of layers is plotted in Figure 12. The elastic modulus remains constant, as expected due to the thickness of the ZrN film. Under higher loads, we should expect to see a difference, similar to what Burghard et al. found for thinner ceramic layers [8]: higher difference in the plastic behavior (hardness) than with the elastic modulus.

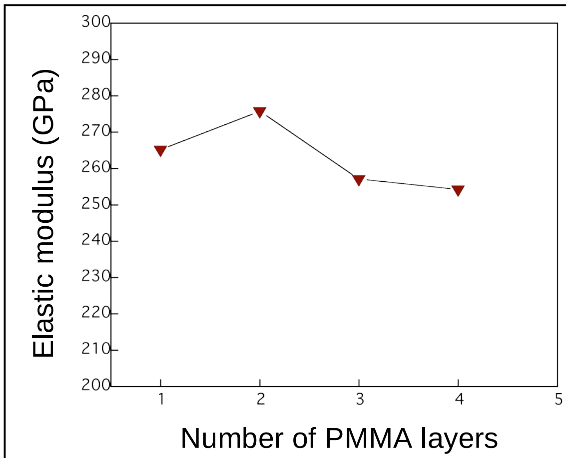

Figure 12. Elastic modulus as a function of number of PMMA layers for a ZrN/PMMA multilayered structure.

SUMMARY OF THE RESULTS

In the present paper we had set-up two physical vapor deposition methods in order to prepare zirconium nitride (ZrN) and polymethylmethacrylate (PMMA) multilayer composites. For the ZrN thin films we employed DC magnetron sputtering while for the PMMA polymeric layers a pulsed laser deposition (PLD) technique was used in a sequential way in the same growth chamber without breaking the vacuum. The ZrN films showed nanocrystalline columnar growth on the silicon substrates or the PMMA nanolayer. High resolution SEM analysis at the inorganic/organic interface revealed well formed inorganic films which are separated by the polymeric layer (30-90 nm). Hardness values of ~ 20 GPa are measured on both the ZrN single film and the ZrN/PMMA composite. The elastic modulus values were independent of the number of polymer layers.

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